

# Harmonic Vibrational Excitations in Disordered Solids and the "Boson Peak"

Walter Schirmacher

*Physik-Department E13, Technische Universität München, D-85747 Garching, Germany*

Gregor Diezemann

*Institut für physikalische Chemie, Universität Mainz Wellerweg 15, D 55099 Mainz, Germany*

Carl Ganter

*Physik-Department E13, Technische Universität München, D-85747 Garching, Germany*

We consider a system of coupled classical harmonic oscillators with spatially fluctuating nearest-neighbor force constants on a simple cubic lattice. The model is solved both by numerically diagonalizing the Hamiltonian and by applying the single-bond coherent potential approximation. The results for the density of states  $g(\omega)$  are in excellent agreement with each other. As the degree of disorder is increased the system becomes unstable due to the presence of negative force constants. If the system is near the borderline of stability a low-frequency peak appears in the reduced density of states  $g(\omega)/\omega^2$  as a precursor of the instability. We argue that this peak is the analogon of the "boson peak", observed in structural glasses. By means of the level distance statistics we show that the peak is not associated with localized states.

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A ubiquitous and rather intriguing feature in the physics of glasses is the anomalous behavior of the low-frequency part of the vibration spectrum and the corresponding thermal properties [1–3]. While the origin of the linear low-temperature specific heat is commonly attributed to the existence of double-well potentials or two-level systems [4], there is still considerable debate about the so-called "boson peak". This peak shows up in the density of states (DOS)  $g(\omega)$  as an excess contribution, compared to the usual Debye behaviour ( $g(\omega) \propto \omega^2$ ). It is taken as being responsible for a number of features observed in specific heat and thermal conductivity measurements, as well as in Raman or neutron scattering data [1–3,5–8]. The boson peak seems also to persist at elevated temperatures. Here its relation to the liquid-glass transition and the corresponding relaxation dynamics is a matter of discussion [9–13]. Due to the development of new experimental techniques allowing to perform Brillouin scattering measurements in the THz range [14–17], as well as pertinent molecular dynamics simulations [18–22] the question concerning the nature of the modes in the boson peak region has gained much additional interest recently.

Several models have been formulated to explain the physical origin of the boson peak. In the soft-potential model [23,24] the existence of anharmonic localized vibrations is postulated to be an intrinsic and essential property of amorphous systems. The scattering of propagating phonons by these modes is then taken as the origin for the excess DOS in the boson peak region.

Another, almost orthogonal approach considers harmonic degrees of freedom solely. Here the scattering of phonons is associated with the disorder in the force constants, or, equivalently, spatially fluctuating elastic constants [25]. The first contribution in this direction has been the phonon-fracton approach [26,27], in which harmonic vibrational excitations on a percolating lattice were considered. However, a numerical simulation of this model [27] showed that the crossover from propagating modes (phonons) to localized fractal excitations (fractons) does not lead to an excess DOS, although calculations using the coherent potential approximation (CPA) [28,29] had predicted such an excess. Moreover, there is no experimental evidence for spatially fractal behaviour of bulk glasses.

More realistic disordered coupled harmonic oscillator models work in terms of a continuous distribution of force constants. Calculations of the vibration spectrum of such a model with a specific force constant distribution have been performed in effective medium approximation (EMA, amorphous version of the CPA) [30–33]. In these calculations an excess contribution in the DOS appears in the frequency regime, where the phonon mean free path becomes comparable to the wavelength. However, for this model the existence of the excess DOS has not yet been checked numerically.

Another interesting contribution to the boson peak discussion [12] comes from the mode-coupling theory [34] of the liquid-glass transition. In the idealized glass state a maximum in the density fluctuation spectrum at finite frequencies is predicted which is associated with inhomogeneously broadened harmonic oscillations. Experimental measurements exhibiting a crossover from relaxational to vibrational dynamics [6] have been described successfully in terms of this theory [13].

Calculations for harmonic vibrational excitations in liquids, performed numerically [35,19], as well in EMA [36], can hardly contribute to the present debate, because the Hamiltonians considered are instable [37].

In the present letter we investigate the properties of a simple model for vibrational excitations of disordered systems and show that excess low-frequency modes are present if the system is almost unstable. The model consists of a set of coupled scalar harmonic oscillators placed on a three-dimensional simple cubic lattice with lattice constant  $a=1$ . The coupling among the oscillators is modelled by nearest-neighbor force constants  $K_{ij}$ , which are treated as independent (quenched) random variables, chosen according to a distribution with density  $P(K_{ij})$ . The corresponding Hamiltonian has off-diagonal elements  $\mathcal{H}_{ij} = K_{ij}$  and diagonal elements  $\mathcal{H}_{ii} = -\sum_{j \neq i} K_{ij}$ . For a stable system all eigenvalues  $\lambda_i = -\omega_i^2$  are negative,  $\omega_i$  denoting the vibrational eigenfrequencies. In all calculations we have chosen a truncated Gaussian distribution with  $P(K) = P_0 \exp\{-(K - K_0)^2/2\sigma^2\}\theta(K - K_{\min})$ . Here  $\theta(x)$  denotes the step function,  $P_0$  is a normalization constant,  $K_0$  and  $\sigma$  denote the maximum value and the width, respectively. In our calculations we set  $K_0 = 1$ . The lower cut-off of the force constant distribution is denoted by  $K_{\min}$ . This cut-off is introduced to allow for the study of strongly disordered systems with a restricted amount of negative force constants.

The model defined in this way has been analyzed, both, numerically by diagonalizing the Hamiltonian matrix, as well as in CPA. The DOS obtained from both methods are in excellent agreement with each other, except near the point of instability.

For the numerical treatment we considered a cubic box of size  $L$  and imposed periodic boundary conditions. The resulting  $L^3 \times L^3$  Hamiltonian matrix was diagonalized using the NAG-LAPACK routine DSYEV. The distribution of eigenvalues exhibits gaps due to finite-size effects. In order to eliminate these effects we calculated the integrated density of levels  $F_L(\lambda) = \sum_i \theta(\lambda - \lambda_i)$  for a given size  $L$ , smoothed this function and averaged it over different sizes, ranging from  $L = 10$  to  $L = 14$ . This procedure yielded a function  $\bar{F}(\lambda)$ , the derivative of which gives the density of levels  $n(\lambda) = d\bar{F}(\lambda)/d\lambda$ . From this the vibrational DOS follows as  $g(\omega) = 2\omega n(-\omega^2)$ .

For an approximate solution of our model we have used the single-bond CPA [38–40]. This theory is formulated in terms of a frequency-dependent force constant ("self energy")  $\Gamma(\omega)$ , which can be visualized as the inverse of an acoustic dielectric function. The frequency-dependent complex sound velocity  $v(\omega)$  is given by  $\Gamma(\omega) = v(\omega)^2$ . In CPA the quantity  $\Gamma$  is determined self-consistently in terms of the local Green's function  $G_0(z) = \sum_{k_x k_y k_z} [z + 6 - 2(\cos k_x + \cos k_y + \cos k_z)]^{-1}$  of the ordered cubic lattice (the sum runs over the Brillouin zone and  $z = -\omega^2 + i\epsilon$ ) as follows:

$$\left\langle \frac{\Gamma(z) - K_{ij}}{1 - (\Gamma(z) - K_{ij})(1 - z\tilde{G}_0(z))/3\Gamma(z)} \right\rangle = 0 \quad (1)$$

with  $\tilde{G}_0(z) = G_0(z/\Gamma(z))/\Gamma(z)$  and

$\langle A \rangle = \int dK_{ij} P(K_{ij}) A(K_{ij})$ . The DOS is obtained from a numerical solution of eq. (1) and use of the relation  $g(\omega) = -(2/\pi)\omega \text{Im}\{\tilde{G}(z)\}$ .

Preliminary calculations showed that without lower cutoff (i. e.  $K_{\min} = -\infty$ ) the system becomes unstable for  $\sigma \approx 0.6$ . In order to be able to study a strongly disordered system we have set  $\sigma = 1$  and varied the cutoff  $K_{\min}$  which controls the amount of small and negative force constants. Fig. 1 shows results of such calculations. The excellent agreement of the CPA calculations with the numerical analysis [41] (except for the immediate vicinity of the instability) indicates both the reliability of the CPA and the correctness of the procedure utilized for the elimination of finite-size effects in the numerical work. As  $K_{\min}$  decreases from positive to negative values, the peak in  $g(\omega)/\omega^2$  shifts towards smaller frequencies. At the same time the peak intensity increases. In CPA the system becomes unstable for  $K_{\min} = -0.85$ , whereas in the numerical calculation the instability already occurs near  $K_{\min} = -0.6$ . The low-frequency peak thus plays the role of a precursor of the instability introduced by the presence of small and negative force constants. We therefore conclude that a low-frequency peak observed in the reduced DOS of a disordered harmonic system indicates that it is almost unstable.

Another quantity of interest, in particular in the context of thermal conductivity data in structural glasses [3,42], is the mean free path of the phonons  $\ell$ . Within the CPA treatment the mean free path can be identified with the decay length of the wave intensity  $|\exp\{i\omega r/v(\omega)\}|^2$  and is therefore given by

$$\ell^{-1}(\omega) = \frac{2\omega \text{Im}\{v(\omega)\}}{|v(\omega)|^2} \quad (2)$$

and behaves as  $\ell^{-1} \propto \omega^4$  for  $\omega \rightarrow 0$  (Rayleigh scattering).

In fig. 2 we have plotted the reduced quantity  $\ell^{-1}(\omega)/\omega^4$  for the same force constant distributions as in fig. 1. It is seen that the mean free path strongly decreases with the amount of small and negative force constants. In scattering experiments the decrease in  $\ell(\omega)$  would show up as an increasing width of the Brillouin peaks. The  $\omega^4$  dependence of

$\ell(\omega)$  levels off near the frequency where the reduced DOS has its maximum. It has already been demonstrated in the literature that such a frequency dependence of  $\ell$  is capable to explain the plateau in the thermal conductivity [3,32]. One sees from fig. 2 that for  $K_{\min} = -0.6$  (almost unstable case)  $\ell$  is in this frequency range of order unity. Since the real part of  $v(\omega)$  and  $\omega$  are of order unity as well the mean free path becomes comparable to the wavelength, in which case the phonons may become localized according to the Ioffe-Regel criterion [42].

Therefore we were interested in the question as to whether in our model the vibrational states are localized. This can be checked by an investigation of the level statistics [43]. If we define normalized eigenvalues by  $\epsilon_i = \bar{F}(\lambda_i)$  a histogram of the distances  $s_i = |\epsilon_i - \epsilon_{i+1}|$  should yield a distribution according to the Gaussian orthogonal random matrix ensemble (GOE)  $P(s) = \frac{1}{2}\pi s \exp\{-\pi s^2/4\}$  in the case of delocalized states, whereas one expects a Poissonian distribution  $P(s) = \exp\{-s\}$  for localized states. This is due to the fact, that the delocalized states show level repulsion, whereas the localized ones do not.

In fig. 3 we show a representative set of the level distance statistics of our calculated spectra. It is clearly seen that they universally follow the GOE statistics. We therefore conclude that the states in our model are all delocalized for the force constant distributions considered, also in the vicinity of the instability.

When comparing our results with real three-dimensional disordered systems like glasses a few comments are in order. We have treated a scalar model and thus ignored the vector character of the phonons completely. We believe, however, that our model already is able to mimic the behavior of transverse phonons in a glass. If the vector character is taken into account, one would expect an even stronger scattering due to the admixture of longitudinal degrees of freedom. We therefore believe that our model underestimates the intensity of the boson peak somewhat. We expect also that in a modified version of our model the states near the boson peak may become Anderson-localized near the borderline of stability. Therefore we have to state that in a real glassy system it still remains an open question, whether the modes associated with the boson peak are localized or delocalized. Our model shows, however, that is not necessary to postulate the existence of localized states or strongly anharmonic effects to obtain an excess contribution in the DOS.

As we have treated only harmonic interactions the effects associated with the glass-liquid transformation [12,34] are outside the scope of the present model.

In conclusion we have solved a simple model of coupled harmonic oscillators, both, numerically and in coherent-potential approximation. Near the point of instability the model exhibits a low-frequency peak in the reduced density of states  $g(\omega)/\omega^2$ , which we view as the analogue to the boson peak observed in structural glasses.

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FIG. 1:  
Reduced DOS  $g(\omega)/\omega^2$  against frequency for force constant distributions with  $\sigma = K_0 = 1$  and different lower cutoffs  $K_{\min}$ . The symbols represent the numerical diagonalization, the full lines the CPA results. The agreement is achieved without any adjustable parameters.

FIG. 2:  
Reduced inverse mean free path  $\ell^{-1}/\omega^4$  calculated in CPA according to (2) for the parameters of fig. 1.

FIG. 3:  
Level distance statistics for the distributions with negative values of  $K_{\min}$ . Since they follow the statistics of the Gaussian orthogonal ensemble (GOE), the corresponding states are delocalized.

Fig. 1

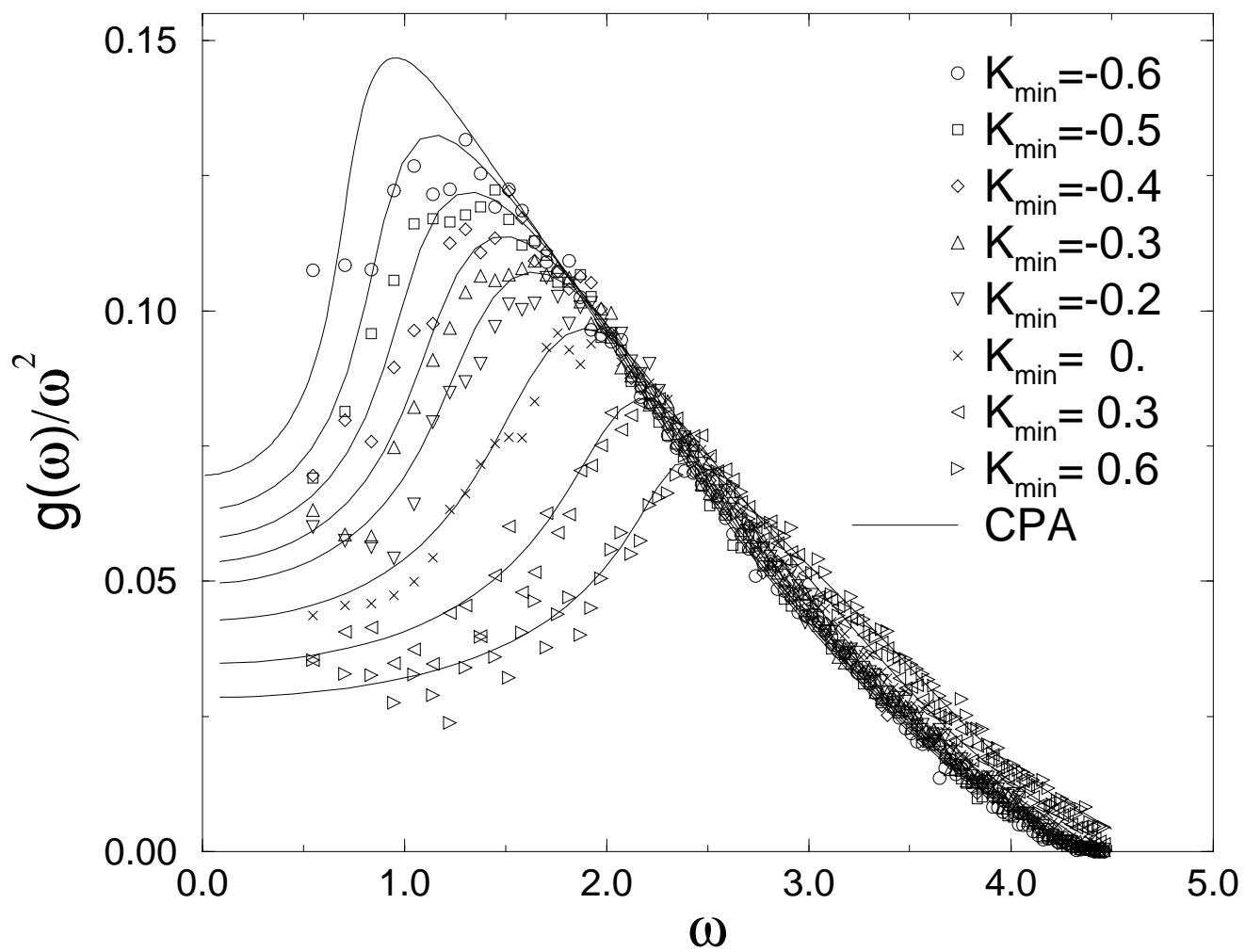


Fig. 2

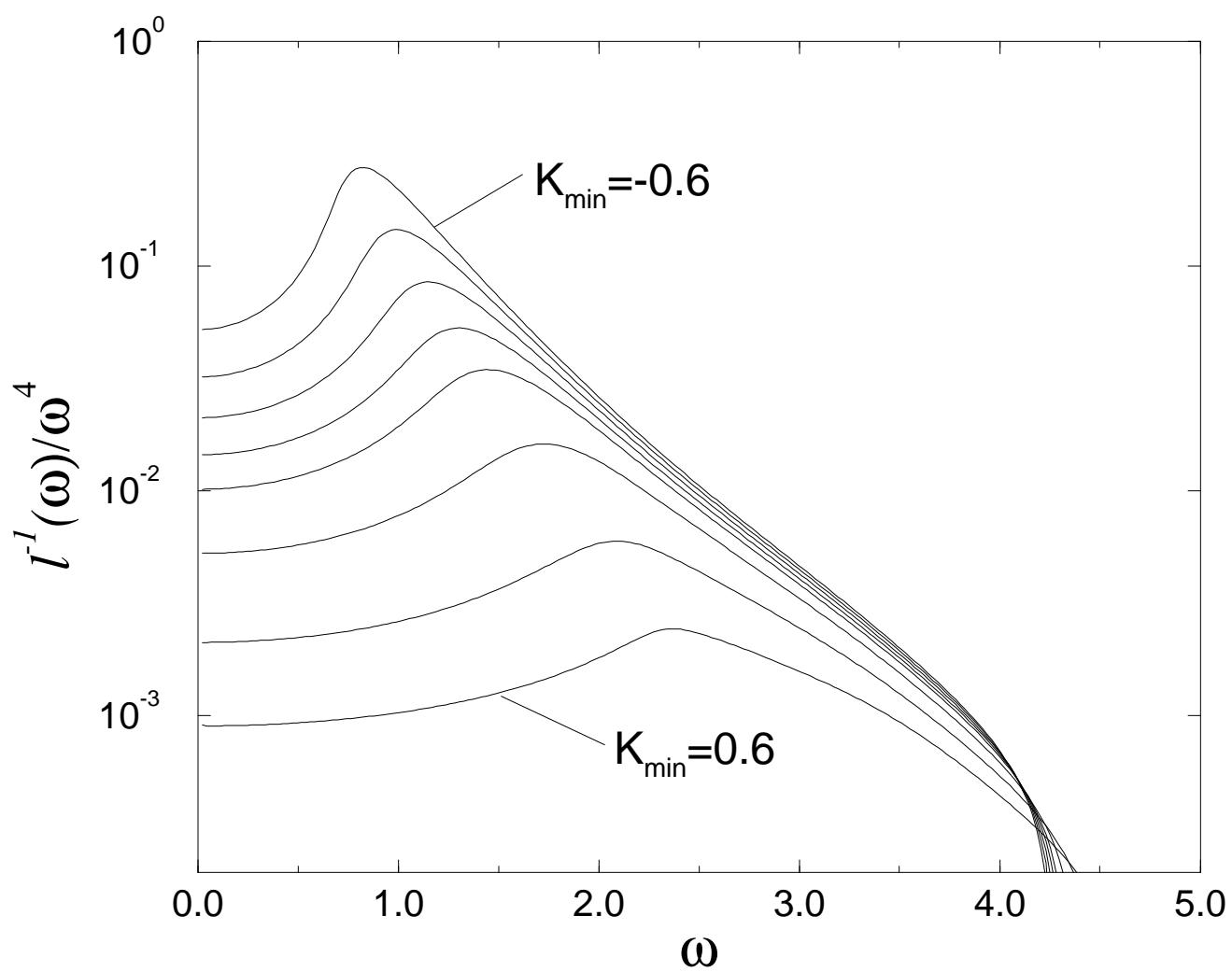


Fig. 3

